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THE EFFECT OF SOL-GEL FILM COMPOSITION ON DIFFUSION OF GLASS SUBSTRATE COMPONENTS

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The distribution of sodium, calcium, and silicon in three-component iron-containing thin films was investigated using the method of secondary ion mass-spectroscopy. A relationship between the diffusion intensity, on one hand, and the composition, propensity to crystallization of the coating, and acidity of the film-forming solution, on the other hand, was established. The effect of diffusion processes on the physical and physicochemical properties of films was assessed.

Oxide sol-gel coatings are amorphous materials that are close to glass in their properties [1]. It is known that the physical and physicochemical properties of glass mostly depend on its composition and on the glass making and annealing conditions [2].

Sol-gel films of small thickness (100 – 1000 Å) are deposited on the surface of thick (3 – 10 mm and more) glass substrates, therefore migration of the glass components has a great effect on the final composition and properties of the coatings.

The thermally polished glass selected as a substrate in our studies is a traditional $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$ three-component system modified by small quantities of oxides of bivalent and trivalent elements. The diffusion of low-refractive sodium and silicon oxides is the main reason for the decrease in the refractive index and mirror reflection coefficient of the coating, as well as modification of a number of the physical and physicochemical properties of the coating compared to their expected values.

The purpose of the present work is a preliminary assessment of the effect of thin film composition on the intensity of diffusion of Na_2O , CaO , and SiO_2 from the glass substrate.

Three-component sol-gel coatings of the following molecular composition (by synthesis) were studied: $80\text{R}_x\text{O}_y \cdot 20\text{R}'_x\text{O}_k$ (where R, R' are Si, Ti, Zr, La, Bi, In, Sb). In each of them 20 wt.% Fe_2O_3 was introduced (above 100%). The films were deposited on the surface of thermally polished glass sheets via water-alcohol solutions whose total mass content of film-forming oxides was 2.5%. The coatings were fixed by firing at 450°C for 30 min.

Film-forming solutions (FFS) were prepared from titanium and silicon alkoxides, zirconium oxychloride, ferrous chloride, and oxides of bismuth, lanthanum, indium, and antimony dissolved in hydrochloric acid (i.e., actually chlorides of the elements listed).

The following physical and physicochemical properties of the films were determined: refractive index (LEF-3M1

ellipsometer); mirror reflection coefficient (Pulsar spectral colorimeter); Vickers microhardness (PMT-3 instrument); chemical resistance to 0.1 N solution of hydrochloric acid [3]. The distribution of silicon, calcium, and sodium ions at the boundary dividing film and the substrate was investigated by the secondary ion mass-spectrometry (MS-72 instrument). The content of Na_2O , CaO , and SiO_2 in the sol-gel coating was calculated semiquantitatively based on the content of the oxides mentioned in the glass, the coating thickness, and the distribution profile of analogous cations as described in [4].

Table 1 gives the molar content of oxides in the film, taking into account diffusion, amount of hydrochloric acid required for preparation of 100 ml of stable FFS, molar content of Na_2O , CaO , and SiO_2 in the coating, confidence intervals of distribution of the actual refractive indexes, mirror reflection coefficient, Vickers microhardness, chemical stability, and molar content of oxides in the tetrahedral $[\text{RO}_4]$ and non-tetrahedral $[\text{RO}_x]$ forms.

In the calculations, it was taken into account that tetravalent elements (silicon, titanium, zirconium) are capable of forming tetrahedrons combined in a solid and strong elemental oxygen skeleton in the glass. Introduction of alkali and alkaline-earth metal oxides (Na_2O , CaO) disturbs its integrity and strength, since $\text{R} - \text{O} - \text{R}$ bonds (where R is Si, Ti, and Zr) rupture and form non-bridging oxygen ions. If the glass contains sesquioxides (e.g., B_2O_3 , Al_2O_3), the sodium and calcium ions cease to act as depolymerizing agents. Boron and/or aluminum ions acquire oxygen from sodium and/or calcium oxide, pass into four coordination, and form a single structural lattice together with the oxides of tetravalent elements [2, 5]. It can be assumed that similar transformations happen to the oxides contained in the films investigated in the present work: In_2O_3 , Sb_2O_3 , La_2O_3 , and Bi_2O_3 . In that case, the molar content of trivalent elements in coordination $[\text{RO}_4]$ would be numerically equal to the molar content of sodium and calcium oxides diffusing from the glass into the coating, and the number of elements mentioned

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in other coordinations $[RO_x]$ is determined by the difference between the total molar contents of R_2O_3 and $[RO_4]$.

Thus, four-coordinated elements strengthen amorphous material by being incorporated themselves into the integrated lattice, while non-tetrahedral structural units weaken the bonds because they cannot be incorporated into the lattice.

An analysis of the data from Table 1 established that the intensity of diffusion of substrate elements into the film depends on the amount of hydrochloric acid in the respective solution, the size of the film cations, and the presence of crystals in the coating.

The effect of the solution pH (related proportionately in the first approximation to the amount of hydrochloric acid in the solution) is clearly observed in $80La_2O_3 \cdot 20R_xO_y$ series: 74% of the oxides from the glass substrate diffuse in $La_2O_3 - Sb_2O_3$ coating (th molar content is indicated), 35% of the oxides diffuse in $La_2O_3 - Bi_2O_3$ film, and only 31% of the oxides diffuse in the coating of the $La_2O_3 - SiO_2$ system. This correlates with the HCl content in the FFS of the compositions mentioned above and is due to various degrees of glass substrate destruction under the effect of acid solutions of various concentrations.

The amount of hydrochloric acid in the two FFS having similar compositions ($In_2O_3 - ZrO_2$ and $In_2O_3 - TiO_2$) is identical (see Table 1). Yet, 82% of the $Na_2O + CaO + SiO_2$ diffuses from the glass substrate in the first film, and only

41% diffuses in the latter film. It is probably related to the difference in the size of the zirconium (0.161 Å) and titanium (0.146 Å) atoms.

This factor is often the predominant one. It is supported by the correlation of the following films: $Sb_2O_3 - La_2O_3$ and $Sb_2O_3 - SiO_2$; $Sb_2O_3 - Bi_2O_3$ and $Sb_2O_3 - In_2O_3$; $In_2O_3 - La_2O_3$ and $In_2O_3 - SiO_2$; $La_2O_3 - ZrO_2$ and $La_2O_3 - TiO_2$. For each of the pairs listed, the concentration of HCl is lower in the first FFS than in the second FFS, and diffusion from the substrate into the first film is greater than diffusion into the second film because of the difference in the atom size between lanthanum and silicon, bismuth and indium, zirconium and titanium.

The emergence and (or) strengthening of the crystallization process weakens migration of the components from the substrate [6]. Therefore, in the film series containing Sb_2O_3 , minimum diffusion is observed for $Sb_2O_3 - La_2O_3$ (43%) and $Sb_2O_3 - SiO_2$ (26%) compositions due to crystallization. This is the cause of the similar intensity of oxide penetration from the glass substrate into the crystal-containing ($La_2O_3 - Sb_2O_3$) and amorphous ($La_2O_3 - ZrO_2$) films, although the correlation of their compositions (the radii of antimony and zirconium atoms are practically equal) and FFS acidity (the HCl content ratio is 1:4) gave reason to expect significantly stronger diffusion into the $La_2O_3 - Sb_2O_3$ coating.

TABLE 1

Film	Molar content, %							Diffused, %	HCl concentration, ml per 100 ml of FFS	Molar content, %		Surface area under distribution curve, mm ²		Index of refraction		Mirror reflection coefficient, %	Vickers microhardness, MPa	Chemical stability, %
	R_2O_3	R_xO_y	Fe_2O_3	Na_2O	CaO	SiO_2	$Na_2O + CaO$											
										$[RO_4]$	$[RO_x]$	$Na_2O + CaO$	$SiO_2 \cdot 10^2$	estimated value	actual value			
1	21Sb ₂ O ₃	5ZrO ₂	8	16	23	27	39	66	5.2	61	0	637	13	1.80	1.86 - 1.81	22.7 - 21.5	6730 - 6510	12 - 5
2*	45Sb ₂ O ₃	12SiO ₂	17	10	3	13	13	26	7.2	38	49	461	10	1.75	1.86 - 1.81	24.0 - 16.0	6430 - 6170	49 - 35
3	8Sb ₂ O ₃	3Bi ₂ O ₃	4	6	0	79	6	85	6.7	85	9	466	16	No data				
4	20Sb ₂ O ₃	5In ₂ O ₃	9	37	29	0	66	66	7.7	34	0	546	12	The same				
5*	34Sb ₂ O ₃	8La ₂ O ₃	15	36	7	0	43	43	6.8	43	14	490	13	1.78	1.99 - 1.89	28.0 - 19.0	6600 - 6320	71 - 66
6	11In ₂ O ₃	4ZrO ₂	4	2	3	76	5	81	7.5	85	10	519	16	1.79	1.74 - 1.70	22.0 - 14.0	6630 - 6320	64 - 58
7	22In ₂ O ₃	6SiO ₂	8	16	7	41	23	64	8.0	70	7	460	12	1.77	1.72 - 1.69	19.7 - 16.3	6690 - 6310	60 - 44
8	12In ₂ O ₃	4La ₂ O ₃	16	5	4	59	9	68	7.4	68	23	402	17	1.72	1.58 - 1.54	10.0 - 9.0	6890 - 6540	44 - 27
9	36In ₂ O ₃	10TiO ₂	13	28	13	0	41	41	7.5	51	8	464	13	1.75	1.60 - 1.48	10.7 - 9.9	6680 - 6450	65 - 7
10*	41La ₂ O ₃	10SiO ₂	18	15	6	10	21	31	8.1	41	38	399	13	No data			6400 - 6110	68 - 61
11*	35La ₂ O ₃	10Bi ₂ O ₃	20	12	3	20	15	35	8.6	35	50	400	13	The same			7000 - 6780	81 - 43
12*	15La ₂ O ₃	4Sb ₂ O ₃	8	11	5	57	16	73	9.5	73	11	454	15	"			7000 - 6800	No data
13	14La ₂ O ₃	22ZrO ₂	15	3	6	40	9	49	1.7	71	20	429	14	No data				
14	14La ₂ O ₃	57TiO ₂	12	14	3	0	17	17	3.6	74	9	430	12	1.88	1.86 - 1.81	23.8 - 22.8	6160 - 5950	32 - 11

* According to light microscopy data, crystal inclusions are present in the film.

The abnormally low content of sodium, calcium, and silicon oxides in the Sb_2O_3 – SiO_2 film (26%) versus the In_2O_3 – SiO_2 coating (65%) is due to crystallization of the former composition, since the insignificant difference in size between antimony and indium atoms (only 0.3%) and acidity of the respective FFS (HCl content differs by 3%) could not cause a more than two times difference in the diffusion degree.

Thus, migration processes at the boundary between the substrate (glass) and sol-gel coating intensify with an increase in FFS acidity and the size of the atoms in the coating. The emergence or strengthening of crystallization weakens diffusion.

A relationship close to inverse (Table 1) was observed between the quantity of penetrating sodium and calcium oxides on one hand, and SiO_2 on the other hand. In our opinion, it can be accounted for by structural transformations of sesquioxides forming part of the coating. As was noted earlier, R_2O_3 is capable of creating lattice-forming tetrahedrons only in the presence of oxides which easily release oxygen, such as Na_2O and CaO . It can be apriori assumed with a certain degree of probability that film-forming skeletons consisting of sesquioxides $[\text{RO}_4]$ and tetravalent oxides are incompatible due to certain internal reasons and have difficulty in being incorporated in a single structural lattice.

It ensues from Table 1 that the actual refractive index of any coating nearly always differs from the estimated one. This is due to penetration of "alien" silicon, sodium, and calcium oxide with refractive indexes of 1.475, 1.590, and 1.830, respectively, into the film. This is the cause of the abnormally low mirror reflection coefficient of the films obtained from oxides with high refractive indices: Na_2O — 1.590; CaO — 1.890; In_2O_3 — 2.010; La_2O_3 — 2.080, Sb_2O_3 — 2.070, Bi_2O_3 — 2.450; SiO_2 — 1.475; TiO_2 — 2.130; ZrO_2 — 2.170 [2].

The method chosen for assessing the chemical stability of coatings [3] implies measuring the film thickness using the ellipsometric method before and after the action of an etching reagent, and subsequent simple calculations. This method is rather crude, since it is often difficult or even impossible to perform the ellipsometric measurement before and after etching in the same spot of the film. This is responsible for the great scattering in the chemical stability values of a particular coating. In comparing films with clearly different chemical stability (Table 1), one can notice a correlation between this parameter, on one hand, and the presence of crystals, concentration of $\text{Na}_2\text{O} + \text{CaO}$ and SiO_2 , amount of $[\text{RO}_4]$ and $[\text{RO}_x]$, and the size of the atoms in the coating on the other hand. The parameters that reduce chemical stability are: beginning or strengthening of crystallization and increase in the amounts of $\text{Na}_2\text{O} + \text{CaO}$ and $[\text{RO}_x]$. All of the above factors weaken the structure and the bonds between film-forming oxides and facilitate the effect of the etching reagent. An increase in the concentration of SiO_2 and $[\text{RO}_4]$ regularly has the opposite effect.

As for the atom size, the chemical stability of a film deteriorates with an increase in the atom size, due to loosening of the lattice of the film-forming material. It facilitates penetra-

tion of the etching reagent into elemental "pores" of the amorphous material lattice.

Measurements indicate that the thickness of the films investigated (up to 300 Å) is negligible in relation to the thickness of the glass substrate (5–7 mm, i.e. $(5-7) \times 10^9$ Å). In the process of measuring the microhardness by the Vickers method, the diamond indenter of a PTM-3 instrument penetrates into the glass to a depth of 2×10^4 Å (under standard loading of 1 N). This exceeds the film thickness by five or ten times. The greater the content of silicon dioxide in the surface glass layer (including the coating) 2×10^4 Å thick, the harder the product with a sol-gel coating will probably be. Sodium and calcium oxides have the opposite effect [5].

In order to assess this effect, the areas under the distribution curves of SiO_2 , Na_2O , and CaO were calculated from the air-coating boundary to a depth of 20,000 Å. On the whole, it can be assumed that $[\text{RO}_4]$ structure-strengthening fragments (an increase in the area under the SiO_2 distribution curve) will positively characterize the microhardness of a glass article modified with a thin film, and $[\text{RO}_x]$ (an increase in the surface area under the distribution curves of Na and Ca oxides) will have the opposite effect. This assumption is supported by the correlation of coatings with clearly different microhardness values.

Thus, the properties of sol-gel coatings are largely determined by diffusion of elements from the glass substrate. The intensity of migration of sodium, calcium, and silicon from glass is closely related to the FFS acidity, the presence of crystal inclusions, and the atom size. The higher the pH of the solution and the larger the cation size, the more pronounced the diffusion is. Crystals slow diffusion, probably due to the denser structure of the crystal dislocation nucleus [6]. The actual values of the refractive index of sol-gel coatings often differ from the estimated values due to penetration of sodium, calcium, and silicon oxides into the coating. The chemical stability of the film is extremely sensitive to diffusion: SiO_2 improves, and Na_2O and CaO reduce the chemical stability. The presence and amount of $[\text{RO}_4]$ structure-strengthening fragments have a positive influence on the microhardness of articles modified with a sol-gel coating. As the total concentration of silica in the glass layer 10^4 Å thick increases, the microhardness of the articles is improved.

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